

**Replacement of Ozone Depleting and Toxic Chemicals
in Gravimetric Analysis of Non-Volatile Residue**

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Abstract

The standard tests for determining non-volatile residue accretion on spacecraft surfaces and in clean processing facilities rely on the use of halogenated solvents that are targeted for elimination because of their toxic or ozone-depleting natures. This paper presents a literature-based screening survey for candidate replacement solvents. Potential replacements were evaluated for their vapor pressure, toxicity, and solvent properties. Three likely candidates were identified: ethyl acetate, methyl acetate, and acetone. Laboratory tests are presented that evaluate the suitability of these candidate replacement solvents.

Introduction

Control of contamination during processing and integration of spacecraft and launch vehicles is fundamental to insuring mission performance and longevity. Molecular contamination, or non-volatile residue (NVR), is limited by selection of materials and the control of procedures and facilities. Diagnosis of NVR accretion rates is accomplished using witness plates as described ASTM E 1235-88 ("Standard Test Method for Gravimetric Determination of Non-volatile Residue (NVR) in Environmentally Controlled Areas for Spacecraft"). A solvent wipe test documented in USAF Space Systems Division TR-89-63 ("Standard Method for Measurement of Non-volatile Residue on Surfaces") is used to assess hardware cleanliness. These documents, or tailored versions, often define contractual requirements for US spacecraft procurement and launch (Farren *et al*, 1987, 1989; Borson, 1993). These practices rely on the use of dichloromethane (methylene chloride), which is targeted for reduction under the EPA 33/50 program and the Clean Air Act, or a mixture of ethanol with 1,1,1 trichloroethane (methyl chloroform or TCA), which is a "Class 1" ozone depleting chemical.

This paper describes a literature-based screening and laboratory tests of candidate "drop in" replacement solvents for these two tests. To insure a well understood heritage to existing practice, materials' solvent properties, vapor pressure, cleanliness and stability, safety and health issues, and environmental issues were evaluated.

Some general guidelines were followed in selecting the initial set of solvents for screening. Materials that are Class 1 ozone depleting chemicals were not considered as viable replacements for methylene chloride and TCA, for obvious reasons. Only pure materials, not commercial mixtures were considered. Aside from a philosophical desire not to endorse one vendor's mixture over another, relying on a proprietary mixture (which may be subject to unannounced changes in formulation) is undesirable in a standard practice.

These two NVR tests were designed originally to provide a method for comparing facilities and ascertaining facility cleanliness trends, but not necessarily to provide an absolute quantitative determination of a specific type of NVR (Borson, 1994). Therefore, it is important to remember that the goal of finding a replacement solvent for these standard tests is not necessarily to find the "best" solvent for a specific type

of non-volatile residue. Rather, the goal is to find those replacement solvents which most closely match the solvent properties of methylene chloride and the NVR mixture. Initial screening of commonly available organic solvents relies on the "Hansen parameters" characterization of solvents (Barton, 1983). These parameters provide a quantitative representation of the "like dissolves like" rule of thumb so familiar to chemists.

Candidate solvents must have vapor pressures similar to dichloromethane or the TCA/EtOH mixture. If the vapor pressure is too high, the test cannot be completed under standard laboratory conditions. If the vapor pressure is too low, the evaporation process for the gravimetric analysis will take too long, which would result in an unacceptable turn-around rate and risk contamination of the test sample. In the extreme case, the vapor pressure of the solvent may become comparable to the vapor pressure of the "nonvolatile" residue being diagnosed. The NVR tests, as modified, may involve the use of hazardous materials, operations, and equipment. Candidate solvents are screened on the basis of 8 hour threshold limit values, compared with their room temperature vapor pressures.

The overall results of candidate solvent screening are captured in a semiquantitative selection matrix. Three promising candidates for replacement solvents emerge from this screening: ethyl acetate, methyl acetate, and acetone. Controlled evaluations of these candidate solvents, from this laboratory and elsewhere, confirm that they are promising substitutes for halocarbons in standard NVR tests (King and Giordano, 1994; Walter and Parker, 1994).

Solvent Properties Screening

In selecting a solvent for any particular application, chemists generally rely on the rule of thumb that "like dissolves like." For example, a non-polar solute, like a saturated hydrocarbon, is generally best dissolved by a non-polar solvent. Therefore, in selecting replacements for dichloromethane and the NVR solvent blend, one looks for a solvent that is as much "like" them as possible.

One quantitative approach to "likeness" is to use "solubility parameters" to describe the solvents (Barton, 1983). One of the simplest of these parameters, the Hildebrand parameter, is related to the cohesive energy density (cohesive energy per unit volume). The cohesive energy is the energy associated with the net attractive interactions of a material (as compared to an ideal vapor at the same temperature). The cohesive energy density, c , is given by

$$c = -\frac{U}{V} \quad (1)$$

where U is the total molar cohesive energy and V is the molar volume. The units of c are the same as pressure. The Hildebrand parameter, δ , is defined as

$$\delta = c^{1/2} \quad (2)$$

Barton explains the rationale for quantifying solubility in terms of molecular cohesion as follows.

A material with a high δ value requires more energy for dispersal than is gained by mixing it with a material of low cohesion parameter, so immiscibility results. On the other hand, two materials with similar δ values gain sufficient energy on mutual dispersion to permit mixing.

A refinement of the Hildebrand parameter consists of the three-component Hansen parameters. Hansen proposed dividing the total cohesive energy into terms corresponding to dispersion forces, polar forces, and hydrogen bonding, as shown in Eq. (3).

$$\delta_i^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (3)$$

The total Hansen parameter, δ_i , is equivalent to the Hildebrand parameter. The Hansen parameters do not take into account any specific chemical or ionic interactions. They provide an estimate of the properties of mixtures considering only the properties of the individual components. Barton tabulates Hansen parameters for a wide variety of organic chemicals. Figure 1 presents the total parameter, as a bar graph, for a variety of organic solvents.

The Hansen parameters are used here to identify likely candidate replacement solvents.* The most compact comparison is provided by considering the magnitude of the vector (in Hansen parameter space) from methylene chloride or NVR solvent to the candidate solvent. The length of the vector from methylene chloride (DCM) to solvent i is given by

$$d_i^{DCM} = [(\delta_{d_{DCM}} - \delta_{d_i})^2 + (\delta_{p_{DCM}} - \delta_{p_i})^2 + (\delta_{h_{DCM}} - \delta_{h_i})^2]^{1/2} \quad (4)$$

with the distance to NVR solvent defined analogously. Figure 2 shows the vector differences between the various solvents considered and dichloromethane and NVR solvent. The best matches appear to be methyl isobutyl ketone, methyl ethyl ketone, n-butyl acetate, methyl acetate, ethyl acetate, and tetrahydrofuran.

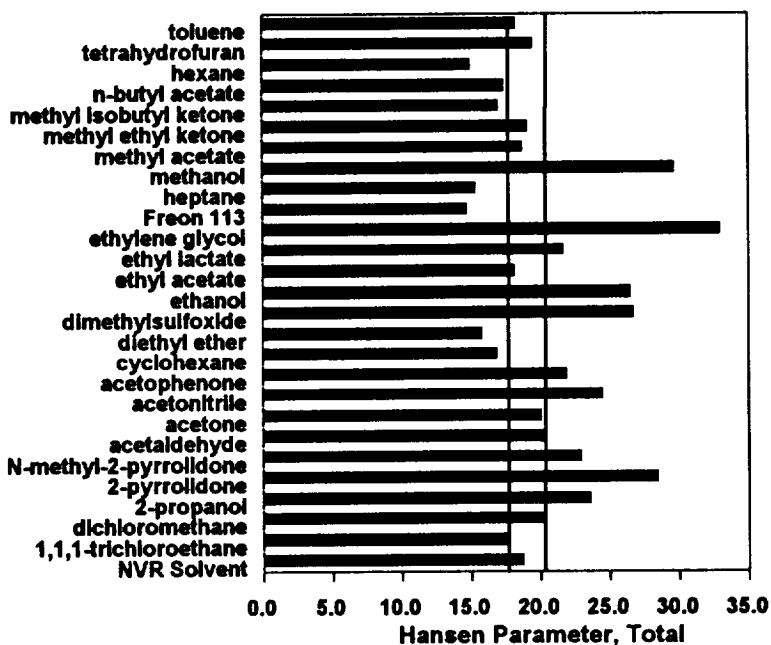


Figure 1. Total Hansen solubility parameter (MPa)^{1/2} for various solvents. The vertical lines show the range from 1,1,1 trichloroethane to dichloromethane.

* The Hansen parameters for NVR solvent were estimated using the volume weighted average of the parameters for 1,1,1 trichloroethane and ethanol.

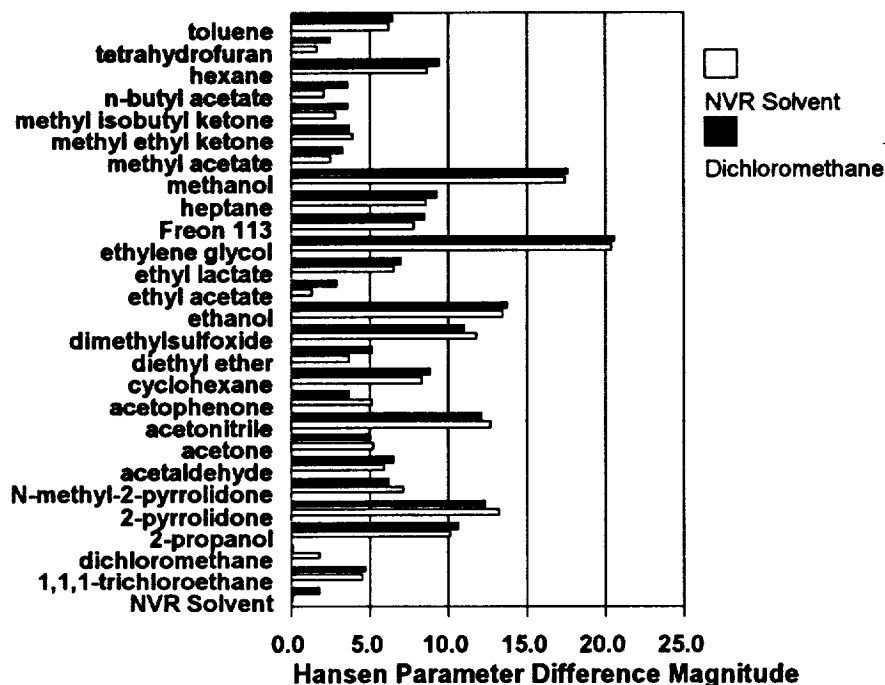


Figure 2 Vector difference in Hansen solubility parameter (MPa)^{1/2} for various solvents compared to dichloromethane and NVR solvent blend.

Vapor Pressure Analysis

A solvent used for non-volatile residue analyses needs to have an appropriate vapor pressure near room temperature. The vapor pressure cannot be so high that the solvent is difficult to handle during rinsing of witness plates or wiping hardware under test. Conversely, the vapor pressure must not be so low that the near-room-temperature evaporation used in the gravimetric analyses takes an excessively long time.* Vapor pressure data were obtained from standard reference works (Lide, 1993; Stecher, 1968; Hill and Carter, 1993). Figure 3 shows the vapor pressure at 25°C for the solvents considered. The two vertical lines indicate the range of useful vapor pressures, as determined from experience. Diethyl ether is about as volatile a material as one would want to handle in the NVR tests. Isopropyl alcohol is about as non-volatile as would be desirable.

This sorting of the solvents considered suggests that diethyl ether, acetone, methyl acetate, tetrahydrofuran, hexane, methanol, methyl ethyl ketone, cyclohexane, acetonitrile, ethyl acetate, ethanol, heptane, and isopropanol are viable candidates for replacing dichloromethane and the NVR mix.

* Note that this requirement for a moderate vapor pressure differs from what one would wish in a cleaning solvent used to wash parts (e.g. in an ultrasonic cleaner). In that case, low vapor pressure (evaporation rate) is a virtue.

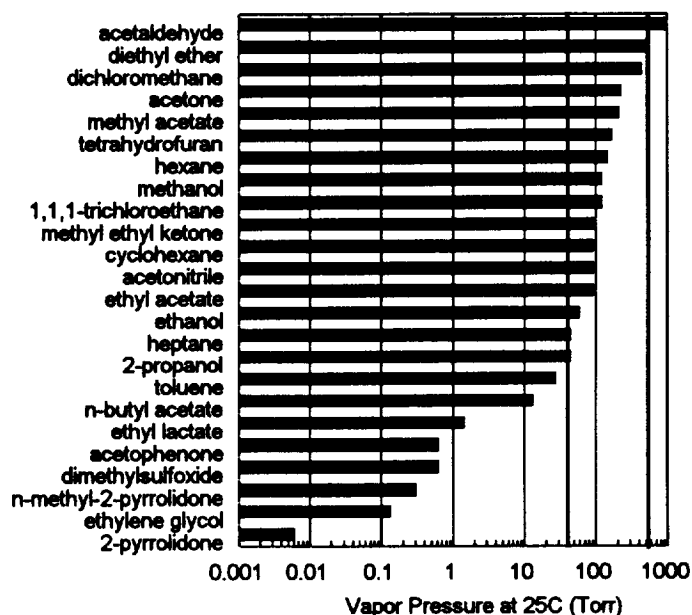


Figure 3 Vapor pressure, in Torr, at 25°C for various solvents. The bold vertical bars indicate the practical working range for NVR analysis.

Hazard Evaluation

Handling organic solvents presents both toxicity and flammability hazards. Almost all conceivable substitutes for the chlorocarbon and chlorofluorocarbons used in NVR analysis present one or both of these hazards. For the purpose of this screening, three figures of merit were examined: (1) the "Threshold Limit Value" for exposure to the material; (2) an inhalation hazard ratio (IHR, defined as the ratio of the saturated vapor concentration at 25°C to the TLV, Walter and Parker, 1994); and (3) the "Flash Point." The inhalation hazard ratio gives a feel for the degree of ventilation required for handling the material in question. Since virtually all the credible short-term replacements for ODC's in the NVR tests are volatile and flammable, the flash point data are not given significant weight in screening potential solvents.

Threshold limit value and flash point data were taken from standard literature sources (Lide, 1993; Lenga, 1988). Table 1 presents the data. TLV's and IHR's with zero values indicate that no TLV data were available for those materials (ethyl lactate, dimethylsulfoxide, and the pyrrolidones). All of the materials examined for which the TLV data are available show a lower IHR and higher TLV than dichloromethane. However, several are more hazardous, by both measures, than 1,1,1 trichloroethane, the more hazardous part of NVR solvent. Table 1 indicates other hazard information. Some of the materials are Class 1 ODC's. Several are on the EPA 17 list. Dimethylsulfoxide is an efficient skin penetrant, making it particularly dangerous when contaminated with other potentially toxic materials. Dichloromethane is a suspected carcinogen. Like most ethers, tetrahydrofuran can decompose into explosive peroxides.

Table 1. Flammability and toxicity hazard assessment for various organic compounds with potential application as NVR solvents.

Solvent	Flash Point	TLV ppm	Inhalation Ratio	Comments
1,1,1-trichloroethane	none	350	451	Class 1 ODC
2-propanol	12	400	140	
2-pyrrolidone	110			no TLV data
acetone	-19	750	386	
acetonitrile	6	40	2888	
cyclohexane	-18	300	396	
dichloromethane	none	50	11184	carcinogen, EPA 17
diethyl ether	-45	400	1806	
dimethylsulfoxide	88			skin penetrant, no TLV
ethanol	12	1000	74	
ethyl acetate	-4	400	288	
ethyl lactate ¹⁰	49			no TLV data
ethylene glycol	111	50	3	
Freon 113	48	1000	434	Class 1 ODC
heptane	-4	400	141	
hexane	-22	50	3816	
methanol	11	200	796	
methyl acetate	-16	200	1375	
methyl ethyl ketone	-6	200	630	EPA 17
n-butyl acetate	22	150	112	
n-methyl-2-pyrrolidone	86			no TLV data
tetrahydrofuran	-14	200	1086	explosion hazard in distillation
toluene	4	50	703	EPA 17

Screening Summary

In this section a semiquantitative combination of screening data is presented, and candidate replacement solvents are identified. The rating scales were designed to give heaviest weighting to the solvent properties, as described by the Hansen parameters. Roughly equal weighting was given to vapor pressure and toxicity.

To put the Hansen parameter analysis on a roughly "one to 10 scale," the following figures of merit for solvent *i* were calculated. [See Eq. (4).] A quantity *Hansen NVR* is defined analogously.

$$Hansen\ DCM = \frac{(20 - d_i^{DCM})}{2} \quad (5)$$

Table 1 shows that virtually all of the solvents under consideration require some degree of ventilation. Therefore, the TLV, not the IHR was used as a rating parameter. To put the data on a 1-10 scale the TLV in volume ppm was divided by 100. If a candidate solvent is on the EPA 17 list, the toxicity rating was arbitrarily assigned a value of -5. Materials for which no TLV data were available received a zero score in this category. A fairly insensitive rating scale for vapor pressure was chosen, the logarithm to base 10 of the 25°C vapor pressure of the material, in Torr. This provided a scale spanning roughly -3 to +3. The individual rating data (rounded to integer values) are presented in Table 2. The

total ratings are shown in Figure 4. The chosen scale provided benchmark values for NVR solvent and dichloromethane of about 25. Five potential solvent replacements rated above 20 on this scale: acetone, diethyl ether, ethyl acetate, methyl acetate, and tetrahydrofuran.

The hazard properties of the two ethers (diethyl ether and tetrahydrofuran) militate against their use in NVR testing. Diethyl ether is at the extreme high end of the range of useful volatility, and presents a severe fire and explosion hazard. Tetrahydrofuran, a cyclic ether, shares a property common to many ethers: it can decompose to form explosive peroxides. "Inhibited" materials are available, but this involves contamination, for example with 250 ppm of butylated hydroxytoluene, which is a solid with a 69°C melting point (Anon, 1992).

In the overall rating, acetone scored among the top candidates. This rating is somewhat misleading in that acetone scored high in the toxicity benchmark, but lower in the solubility benchmarks. Furthermore, it is substantially more polar than the solvents for which replacements are sought. However, this difference may not be as significant as it appears. Barton has pointed out that the polar forces are much less important than hydrogen bonding forces. Testing has shown that acetone is not as effective for some greases as other solvents (King and Giordano, 1994; Walter and Parker, 1994). However, it has some advantages. It is readily available at many laboratories. Indeed, it is already an approved material for use at many US launch sites. (This is a significant bureaucratic hurdle.) Its toxicity and vapor pressure range are attractive. Finally, it has often been mentioned as a candidate for cleaning and NVR diagnosis, so additional data on its utility will likely turn out to be useful.

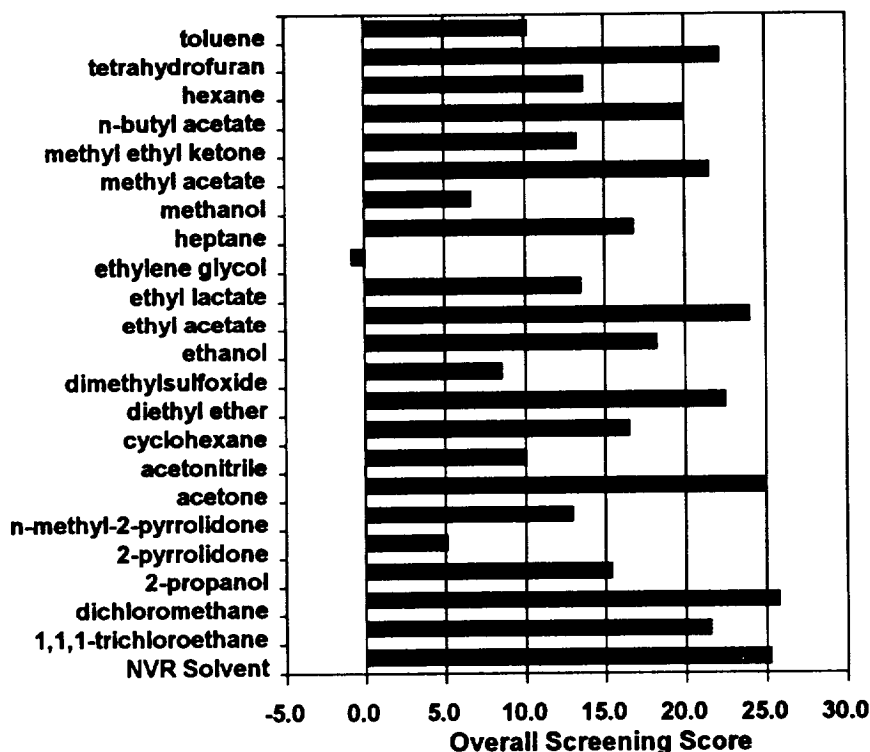


Figure 4 Overall screening score for various current and potential NVR solvents. See text for details.

Table 2. Summary of "figures of merit" for solvent properties, toxicity, and vapor pressure.

Solvent	Hansen DCM	Hansen NVR	Toxicity	Vapor Pressure	Total
NVR Solvent ^a	9	10	4	2	25
1,1,1-trichloroethane	8	8	4	2	22
dichloromethane	10	9	4	3	26
2-propanol	5	5	4	2	15
2-pyrrolidone	4	3		-2	5
n-methyl-2-pyrrolidone	7	6		-1	13
acetone	8	7	8	2	25
acetonitrile	4	4	0	2	10
cyclohexane	6	6	3	2	16
diethyl ether	7	8	4	3	22
dimethylsulfoxide	5	4		0	8
ethanol	3	3	10	2	18
ethyl acetate	9	9	4	2	24
ethyl lactate	7	7		0	13
ethylene glycol	0	0	1	-1	-1
heptane	5	6	4	2	17
methanol	1	1	2	2	7
methyl acetate	8	9	2	2	21
methyl ethyl ketone	8	8	-5	2	13
n-butyl acetate	8	9	2	1	20
hexane	5	6	1	2	14
tetrahydrofuran	9	9	2	2	22
toluene	7	7	-5	1	10

a. Assuming 1,1,1 trichloroethane vapor pressure.

Experimental Results

The first part of experimental testing was to ascertain the availability of solvents of suitable purity for this application. A review of organic chemical vendors revealed that ACS HPLC grade materials are available for both acetates (at < 3 ppm evaporation residue specification) and acetone (< 10 ppm). The price for these solvents is approximately \$20 per liter. Table 3 shows examples of laboratory tests, following the procedure in ASTM E 1235 to evaluate the achieved cleanliness for some samples of the esters, compared to HPLC dichloromethane and "anhydrous" TCA. Note that these data evaluate both the purity of the solvent and the "technique" of the experimenter. The data shown in Table 3 justify the use of the "as received" HPLC grade solvents, without further purification, in the laboratory test program.

The suitability of the candidate replacement solvents is being tested using both adventitious contaminants obtained by exposing witness samples to various controlled and uncontrolled environments and by using samples prepared with known amounts of pure and mixed contaminants. The model contaminants include lubricants used in the Titan IV program, hydrocarbons, siloxanes, and phthalate esters. Test plates of 1 sq. ft. area that can be precontaminated by evaporating prepared solutions were fabricated for controlled surface wipe tests.

Table 4 presents an example of an ASTM E1235-88 stainless steel witness plate test for samples that were exposed in the Aerospace Corp. machine shop for about 1 month, then bagged together for ~3 months. The agreement between the results for the standard solvent and ethyl acetate is strikingly good.

Table 3. Solvent NVR tests, 60 ml samples.

Solvent	Test 1				Test 2			
	Residue (g)	ppm	Mean	Std. Dev.	Residue (g)	ppm	Mean	Std. Dev.
Dichloromethane	0.00007	0.9	0.9	0.1	0.00013	1.6	2.0	0.31
	0.00008	1.0			0.00019	2.4		
	0.00006	0.8			0.00016	2.0		
Ethyl Acetate	0.00026	4.8	4.0	0.68	0.00003	0.6	0.6	0.00
	0.00017	3.1			0.00003	0.6		
	0.00022	4.1			0.00003	0.6		
Methyl Acetate	0.00002	0.4	1.6	1.2	0.00008	1.4	0.7	0.58
	0.00007	1.3			0.00000	0.0		
	0.00018	3.2			0.00004	0.7		
Trichloroethane	0.00034	4.2	3.5	0.56	0.00033	4.1	4.4	0.99
	0.00028	3.5			0.00046	5.7		
	0.00023	2.9			0.00027	3.4		

Table 4. ASTM E 1235 test comparison between dichloromethane and ethyl acetate

Measured Mass (g)	Solvent	
	Dichloromethane	Ethyl Acetate
Sample	0.00093	0.00147
Blank	0.00029	0.00072
NVR	0.00064	0.00075

Table 5 presents results from a controlled surface wipe test experiment. In this case, the test plates were contaminated with an aliphatic hydrocarbon, squalane, dissolved in heptane (certified to an evaporation residue of less than 1 ppm). These initial results are not quite as promising as those for the ASTM test. Further experimentation with a variety of contaminants is clearly required. Also, in performing these tests, it was observed that the methyl acetate evaporated very rapidly, while the wipe was being performed. This observation, and the fact that methyl acetate is somewhat more toxic than the other solvents, may militate against its use for the wipe test.

Table 5. Test results for NVR wipe of test samples pre-contaminated with squalane

Solvent	Applied NVR (g)	Sample NVR (g)	Blank NVR (g)	Test NVR (g)
Methyl Acetate	0.00364	0.00265	0.00110	0.00155
Ethyl Acetate	0.00362	0.00306	0.00218	0.00088
"NVR" Solvent	0.00369	0.00514	0.00209	0.00305

Summary and Conclusions

The standard tests for determining non-volatile residue accretion on spacecraft surfaces and in clean processing facilities rely on the use of halogenated solvents that are targeted for elimination because of their toxic or ozone-depleting natures. A literature-based screening survey for candidate replacement solvents has been described. Potential replacements were evaluated for their vapor pressure, toxicity, and solvent properties. Three good candidates were identified: ethyl acetate, methyl acetate, and acetone.

Laboratory tests have confirmed that commercially available materials, in ACS HPLC grade, are adequate for this task, for the esters. Laboratory testing using model and adventitious contaminants has shown that the esters are promising candidate materials for replacing halocarbons in the standard spacecraft NVR tests. This general conclusion is supported by, other testing of potential NVR and cleaning solvents at Martin Marietta (King and Giordano, 1994; Barrows, 1994) and elsewhere (Walter and Parker, 1994).

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